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APPLICATION UNDER UNITED STATES PATENT LAWS

Invention: PROCESS FOR PRODUCING MARL SLAG

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SPECIFICATION

Process for Producing Marl Slag

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The invention relates to a process for producing marl slags and marl slag cements or mixed components for mixed cements from marl having a basicity CaO/SiO_2 of < 2.0 .

2. Prior Art

When producing cement, calcareous and argillaceous stones, in particular limestone and lime marl, are used as starting materials and burned to cement clinker. The lime contained in the starting materials is completely bound to silicic alumina and optionally iron, thus forming the cement minerals usual to portland cement clinker, such as alite, belite, brown millerite and glass. In order to ensure the desired sintering to cement clinker at comparatively low temperatures of about 1350°C , relatively high-quality starting materials and, in particular, highly calcareous lime marl are required. Lime marl, which usually has a basicity of between 3 and 4 and besides lime also contains SiO_2 , Al_2O_3 and iron oxides, however, occurs in nature not only in the form of relatively high-quality and largely pure lime marl, but rather as a common or low-quality marl in substantially higher amounts. The marl that is substantially more wide-spread is characterized by basicities of between 0.8 and 2 and frequently is found also in the form of argillaceous marl. Those comparatively low-grade, yet substantially more wide-spread starting products in conventional cement production processes cannot be used without expensive purification and lime enrichment procedures and are available in large amounts as cheap raw materials.

Slag cements and, in particular, blast furnace slag cements likewise exhibit hydraulic properties and it has already been demonstrated that, by optimizing the slag chemistry and, in particular, by adjusting basicities and aluminatate contents as well as applying special activation procedures, metallurgical slags will be improved to the extent that they correspond to a

strength development in concrete and are at least equivalent to clinker cement.

Summary of The Invention

The present invention aims to render wide-spread and cheap raw material marls having low basicities apt for economic utilization in the production of slag cements or mixed components for mixed cements while, at the same time, allowing for the adaptation of the desired product qualities to the respective requirements to a high degree. To solve this object, the process according to the invention essentially consists in that in a first process step argillaceous marl or a mixture of marl and clay having a basicity of < 2.0 is dried, preheated and calcined and that, after this, the obtained product in a second process step is melted in a separate melting furnace at higher temperatures than applied in the first process step and is granulated from the melt. Calcination is an endothermic reaction, whereas melting constitutes an exothermic reaction. Due to the fact that argillaceous marl, i.e. relatively low-grade marl, having an elevated Al_2O_3 content or a mixture of low-quality marl and clay having a basicity of below 2 is dried, preheated and calcined in a first process step, it is initially safeguarded that the high amounts of CO_2 released during calcining need not be heated to the temperatures usually required in cement production for sintering. The calcination of hydrate, sulfur and carbonate compounds is, thus, carried out at comparatively low temperatures such that the large gas amounts released occur at accordingly low temperature levels, thus enhancing the thermal efficiency and hence the economy of the process. On account of the relatively low purities of the starting substances used, calcination takes place already at lower temperatures than would be the case with highly pure calcium carbonates. Due to the fact that the obtained product in a second process step is subsequently melted in a separate melting furnace at higher temperatures than in the first process step, there is the possibility to subsequently correct the composition of the melt by any means whatsoever and it is

feasible, by appropriately granulating the melt, to provide the desired glass portion and ensure that any undesired crystallization will be largely avoided during cooling. Drying, preheating and calcining in a first process step at
5 accordingly low temperatures, moreover, allows for the use of substantially more coarse-grained charging substances as compared to known cement clinker sintering processes such that raw material preparation and, in particular, grinding will not be required, as a rule, but the coarse charging stock merely
10 will have to be finely broken. The process according to the invention also calls for a substantially lower heat consumption than the clinker process.

Advantageously, the process according to the invention is
15 carried out in a manner that the first process step is realized in a suspension type heat exchanger, a rotary tubular kiln, a multiple-hearth furnace or a shaft furnace, or in a fluidized bed or cyclone preheating unit. In a particularly advantageous manner, a suspension type heat exchanger may be
20 employed, whereby it is feasible, in particular if a rotary tubular kiln or shaft furnace is employed in the first step, to choose an even coarser particle size of the charging stock, drying, preheating and calcining of a charging material having particle sizes of, for instance, up to 40mm being readily
25 feasible.

In a particularly advantageous manner, the second process step is carried out in a melting cyclone, a rotary tubular kiln or a hearth-type furnace, or in an iron melting oxidation
30 reactor, whereby even the formation of foamed slag may be advantageous if a meltdown oxidation reactor is employed.

What is essential in obtaining the desired cement technological properties, after all, is the adjustment of the
35 slag basicity of the target slag, it being advantageously proceeded in a manner that the target slag is adjusted to a basicity CaO/SiO_2 of between 0.9 and 1.85 by mixing marl and

clay. If, at the same time, an Al_2O_3 content of between 6 and 20 wt.-% is aimed at, a high-quality synthetic blast furnace slag will be obtained, such Al_2O_3 contents being obtainable in a particularly simple manner by using argillaceous marls. When
5 using other marl qualities for the main component, the desired slag chemistry may be adjusted by the aid of bauxite, clays, flue ashes or other industrial waste substances such as, for instance, red muds, sweepings, corundum-containing grinding dusts or refractory break-offs.

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What is also essential for obtaining the desired cement technological properties is, of course, accordingly rapid cooling so as to prevent the formation of crystals. Depending on the basicity of the slag, the slag is characterized by
15 different viscosities, wherein the slag becomes highly viscous, in particular, at basicities of above 1.4, and the formation of crystals can no longer be reliably prevented in conventional granulation processes such as, for instance, during granulation in hot water. In the context of the
20 invention it is, therefore, advantageously proceeded in a manner that the melt at basicities of > 1.4 is sprayed into a granulator and, in particular, a vapor granulator. Spray granulation, in which the cooling of the molten droplets in most cases is effected by nozzling in water or water vapor,
25 may be substantially improved even further in that hydrocarbon is additionally nozzled into the spray granulator. The thermal decomposition of hydrocarbon withdraws heat from the sprayed droplets at a cooling gradient of 10^4 to 10^5 K/s while simultaneously forming high-quality synthesis gas, which, as
30 in correspondence with a preferred further development of the process according to the invention, can be burned in the first process step, because the actual heat demand for calcination arises there.

35 Since, due to the relatively low purity of the starting materials, calcination takes place at relatively low temperatures, the process according to the invention

advantageously is carried out in a manner that the first process step is carried out at temperatures of up to 950° to 1000°C, drying being effected at temperatures of from 100 to 210°C, preheating being effected at 210° to 600°C and
5 calcining being effected at 600° to 1000°C.

In the second process step, in which the slag is melted in order to subsequently solidify under the formation of a glassy consistency, it is advantageously proceeded in a manner that
10 operation takes place at final temperatures of between 1450° and 1550°C.

As already mentioned, the process according to the invention stands out for obviating any cumbersome raw material
15 preparation and, in particular, for not requiring any grinding of the starting materials. Advantageously, the process according to the invention is carried out in a manner that the first process step is realized with finely broken marl having a mean particle size ranging from 20mm to 30mm.

20 In order to further enhance the cement technological properties, it may be proceeded according to the invention in that by-pass dust from the production of clinker is added to the charging material. Since a slag melt is produced within
25 the context of the process according to the invention, it is thus feasible to introduce into the melt the high alkali content contained in the clinker production by-pass dust, a thus formed product being particularly reactive and characterized by high early strengths. Clinker raw materials
30 as are used in the conventional cement production process, as a rule, are characterized by high alkali contents, and the processing of such alkali-rich raw materials, as a rule, constitutes a problem of disposal, which can be solved by the process according to the invention. Also the use of other
35 industrial alkali-containing waste substances, for instance, those from paper and cellulose pulp production, which partially include also high portions of Al_2O_3 , as well as of

organic matter such as lignin, whose calorific value may be utilized, is advantageous.

5 If the melt is to be subjected to a conventional water granulation procedure, its basicity must be lowered to below 1.4, whereby in those cases the Al_2O_3 content of the target slag must be increased accordingly in order to achieve a march of strength similar to clinker, of the end product.

10 In the context of the process according to the invention, the use of charging materials having elevated dolomite contents has no adverse effects, either, it merely having to be taken care that the MgO portion of the charging material is adjusted to below 19 wt.-%. Up to those amounts, magnesium oxide is
15 able to enhance the granulating capacity due to the reduced slag viscosity, which will lead to an increased portion of amorphous or glassy particles.

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20 In the following, the process according to the invention will be explained in more detail by way of exemplary embodiments.

Example 1

25 A marl slag is produced of the charging materials marl and clay. The starting materials had the following directional analysis:

Component (%)	Marl	Clay
Loss on ignition	32.5	12.5
SiO ₂	23	46
Al ₂ O ₃	4	24
Fe ₂ O ₃	2	15
CaO	33	0.72
MgO	3	0.33
SO ₃	1	-
K ₂ O	0.5	-
Na ₂ O	0.2	0.1
TiO ₂	0.4	1
Sum	99.6	99.7
C/S	1.4348	0.0157

The starting materials were supplemented with clinker furnace by-pass dust, whereby the early strength of the marl slag was significantly increased.

In order to adjust the slag basicity CaO/SiO₂ to below 1.4 so as to apply conventional water granulation, the portions of the two components in the mixture were determined as follows with a target basicity of 1.1 having been sought:

$$\text{Marl portion (x)} = \frac{(\text{C/S}) \cdot \text{SiO}_2 (\text{clay}) - \text{CaO} (\text{clay})}{\text{CaO} (\text{marl}) - (\text{C/S}) \cdot \text{SiO}_2 (\text{marl})}$$

$$\text{Marl portion} = \frac{1.1 \cdot 46 - 0.72}{33 - 1.1 \cdot 23} = 6.48$$

Thus, one part of clay was mixed with 6.48 parts of marl, which resulted in a mixture of 86.6 wt.-% marl and 13.4 wt.-% clay. After this, the crude mixture for the intended marl slag had the following composition:

Marl slag	
Component	Portion (%)
SiO ₂	37.4
Al ₂ O ₃	9.6
Fe ₂ O ₃	5
CaO	41.2
MgO	3.8
SO ₃	1.2
K ₂ O	0.6
Na ₂ O	0.3
TiO ₂	0.7
Sum	99.8
C/S	1.1

After drying at 100° to 210°C, preheating at 210° to 600°C and
5 calcining at 600° to 950°C, the dried and calcined product was
drawn off a suspension type heat exchanger and introduced into
a melting cyclone. Within the melting cyclone, the temperature
was adjusted to between 1450° and 1550°C, whereupon the melt
was granulated in hot water.

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In order to reduce the nitrogen oxide portion, it is also
feasible to realize a progressive postcombustion within the
suspension type heat exchanger by blowing in combustion air,
thereby improving the thermal efficiency. The fuel used in the
15 melting cyclone in an alternative process conduct, in which
the melt was ejected into a spray granulator, was formed by
using hydrocarbons during granulation, the cracked gas or
synthesis gas formed having been used as a fuel together with
air in the melting cyclone. Moreover, this method of
20 granulation caused the iron oxide of the slag to be
practically completely metallized and separated by a
subsequent magnetic separation of the slag.

Example 2

Using a rotary tubular kiln in the first process step and a
hearth-type furnace in the second process step, finely broken
5 marl having a particle size of about 25mm was used. The marl
slag had the following composition:

Marl slag	
Component	Portion (%)
SiO ₂	34.6
Al ₂ O ₃	6
Fe ₂ O ₃	3
CaO	49.6
MgO	2
K ₂ O	0.7
Na ₂ O	0.3
TiO ₂	0.6
Sum	96.8

Due to the relatively high basicity of 1.43, the slag was
10 disintegrated by spraying into a spray granulator, whereby a
high portion of fine granulates was obtained. On account of
the high basicity, the high portion of fine granulates was
characterized by a particularly high hydraulic activity. Such
a slag having a basicity of 1.43 could no longer be
15 successfully granulated with hot water, since the portion of
fines, which is important from a cement technological point of
view, was hydraulically inactivated on account of the belite
crystal formation.